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ABSTRACT

Of the 260 million metric tonnes (MMT) of hazardous waste generated in the United States in 1981, only 1.70 MMT was disposed of through incineration. In addition, 3.85 MMT of industrial wastes that could be considered hazardous were burned as fuels in industrial processes. This paper discusses several processes that can be used to convert hazardous waste to energy, namely: combustion of waste in boilers; disposal in industrial boilers; and burning of wastes in lime kilns. Process descriptions will be presented. Projections on energy recovery that could be realized will be described. Applicable test data will be displayed.

INTRODUCTION

The United States generates about 260 million metric tonnes (MMT) of hazardous waste each year. Most of this waste is non-combustible aqueous material. However, the U.S. Environmental Protection Agency (EPA) estimates that as much as 25 MMT of the total United States hazardous waste generation may be capable of being incinerated (1).

Currently, only 1.7 MMT of hazardous waste is disposed of in permitted incinerators which are regulated under the Resource Conservation and Recovery Act of 1976 (RCRA) as amended in 1984. In addition to the hazardous waste which is incinerated under RCRA, 3.5 MMT of industrial waste materials are burned in industrial boilers and 0.35 MMT are burned in other industrial processes such as cement kilns. Under RCRA, the wastes currently disposed of in boilers and industrial processes are considered fuels and not subject to existing RCRA regulations.

Clearly, there is much more room for the use of combustion to dispose of hazardous waste materials. Incineration is a proven technology which has been demonstrated to have the ability to accommodate a wide range of wastes. The 1984 amendments to RCRA, with their sweeping landfill ban provisions, will prompt more intense consideration of combustion as a disposal technique for wastes which have heretofore been subjected to some form of land disposal.

HAZARDOUS WASTE AS FUELS

The primary purpose of an incineration process is to destroy the hazardous materials in such a manner that human health and the environment are not harmed. That is the basic premise behind the RCRA hazardous waste incineration regulations. Controlled high temperature incineration may include some form of heat recovery but that heat recovery is secondary to the waste destruction process and is employed to make the incineration process more fuel efficient.

Incinerators often burn wastes which have little energy value themselves. These wastes include aqueous wastes and waste containing refractory halogenated compounds. In these instances, combustion is achieved by blending the non-combustible waste materials with higher heating value wastes and/or by cofiring the waste materials with fossil fuels.

Wastes that have some fuel value are often burned as fuels in industrial and commercial operations. These processes include boilers, industrial kilns, industrial furnaces, and industrial ovens. Because they utilize the waste materials as fuels, many of these operations, particularly in the industrial sector, are not subject to EPA's RCRA incineration regulations. In fact, wastes that are burned as fuels in industrial processes are currently not considered to be hazardous wastes at all.

Many hazardous wastes contain materials that have significant fuel value. Spent solvents, alcohol bottoms, and waste oils may have energy values approaching those of fossil fuels. In addition, some wastes may contain trace amounts of less combustible highly halogenated materials in a matrix of combustible wastes which yields a mixture that has a significant heating value.

Table 1 lists the heats of combustion for a number of hazardous wastes (2). Table 1 also provides the EPA RCRA waste I.D. and the approximate annual gene-

TABLE 1. HEATING VALUES OF SELECTED HAZARDOUS WASTES

WASTE I.D.	WASTE DESCRIPTION	APPROXIMATE HEATING VALUE KCal/g	Btu/lb	GENERATION Rate 1000 (MT/Y)
	Waste Motor Oil	9.2	16500	3720
F005	Non-Halogenated Solvents	10.0	18000	3915
K001	Wood Preserving Sludge (PAH)	10.6	19000	62
K013	Acrylonitrile Bottoms	4.3	7800	7
K022	Bottom Tars From Phenol Production	8.3	15000	70
K086	Printers Ink Formulations	5.6	10000	25
K087	Coking Tar Sludges	7.8	14000	3

ation rates for the waste for 1982. As can be seen from Table 1, there is considerable energy value to be exploited in some combustible hazardous waste streams. This is particularly the case for the non-halogenated solvents, such as methanol, toluene, and methyl ethyl ketone.

The wastes listed in Table 1 are actual RCRA wastes, whereas the materials that are currently burned in industrial processes are fuels and not subject to RCRA regulations. In most cases, the only difference between RCRA waste materials and RCRA exempted waste fuel is the final disposition of the waste materials. Many of the waste materials that are now burned as fuels in industrial processes have the same composition and characteristics as the wastes listed in Table 1 and would be RCRA wastes if they were not burned as fuels in industrial processes. In fact, most of the wastes that are now being burned as fuels would most likely be classified as F005 solvent wastes if they were not burned as fuels.

Waste oil is a special case. While currently not regulated as a RCRA hazardous waste, this material nevertheless has many contaminants, particularly metals, that could cause it to be classified as a hazardous waste material. EPA has proposed certain restrictions on the marketing and burning for energy recovery of used oils (3). Basically, the proposed regulations place limits on the amounts of arsenic (5 ppm), cadmium (12 ppm), chromium (10 ppm), and lead (10 to 100 ppm) that can be present in used oil that is burned in non-industrial boilers. From Table 1, we can see that used motor oil can be a significant energy source. In fact, approximately 1.5 million metric tonnes of used motor oil is currently burned as a fuel to produce heat or process steam.

INDUSTRIAL APPLICATIONS

Hazardous waste materials can be burned as fuels in a wide range of industrial applications. Processes that have burned or do burn hazardous waste materials as fuels include industrial boilers; ovens and kilns; steel-making furnaces, commercial and industrial boilers; and industrial space heaters.

Many industrial processes present nominal combustion environments that compare favorably with conditions found in hazardous waste incinerators. Table 2 displays combustion zone temperatures and fuel residence times for a number of industrial processes and for hazardous waste incinerators (4).

EPA has tested many of these processes to determine their suitability for burning hazardous waste materials. This discussion will deal in depth with three such applications: waste oil combustion in commercial boilers; hazardous waste combustion in industrial boilers; and hazardous waste combustion in lime kilns.

The performance of all combustors was evaluated against EPA's requirements for hazardous waste incinerators. These requirements are:

- A Destruction and Removal Efficiency (DRE) of 99.99 percent for all Principal Organic Hazardous Constituents (POHCs)
- Particulate emissions may not exceed 180 mg/dscm (0.08 grains/dscf)
- Emissions of hydrogen chloride (HCl) must be no greater than the larger of either 1.8 kg/hr (4 lb/hr) or 1 percent of the HCl in the stack gas.

In addition, pertinent combustion parameters such as CO, CO_2, and O_2 were recorded at each tested facility.

Waste Oil Combustion In Commercial Boilers

While there is considerable overlap, commercial boilers are generally considered to be boilers in the size range of from 0.5 to 20 million Btu/hr. Industrial and utility boilers are commonly considered to be be larger in size than commercial boilers. Approximately 70 percent of the boilers in the United States can be found in this size range (5).

Commercial boilers are of particular interest with regard to waste oil combustion for a number of reasons. These boilers tend to be located at facilities where fuel costs are a much higher percentage of operating costs than at large industrial installations. For example, a nursery might be more interested in waste oil as a fuel than would be a larger chemical manufacturer. Operators of commercial boilers most likely make spot purchases of untreated or poorly characterized waste fuels. Commercial boilers could be expected to provide less efficient combustion because of their generally intermittent mode of operation. In addition, their widespread distribution and their low stack heights make their emissions more proximate to

TABLE 2. OPERATING RANGES OF COMBUSTION PROCESSES

PROCESS	TEMPERATURE RANGE (°C)	RESIDENCE TIME
Liquid Injection Incinerator	650 to 1600	0.1 to 2 Seconds
Rotary Kiln Incinerator	820 to 1600	Liquids and Gases, Seconds; Solids, Hours
Industrial Boilers	870 to 1430	0.1 to 3 Seconds
Cement Kilns	1400 to 1650	Liquids and Gases, Seconds; Solids, Hours
Lime Kiln	680 to 1900	Liquids and Gases, Seconds; Solids, Hours
Brick Tunnel Kiln	260 to 1180	2 to 5 Seconds
Steel Blast Furnace	1100 to 1870	0.5 to 1.5 Seconds
Glass Melting Furnace	620 to 1480	3.0 to 5.0 Seconds

the general population.

Six boilers were selected for the test program. The boilers were thought to provide a representative cross section of the commercial boiler population. The waste oil for each test was obtained from the same 4,000 gallon lot of used automotive oil. The base used oil was spiked with predetermined amounts of selected organic compounds which may be found in typical waste oils and which are considered hazardous waste materials.

Table 3 describes the destruction and removal efficiencies obtained in the test program for the listed spike compounds (6). The DREs that are displayed are the minimums, maximums, and averages achieved across all six boilers.

Since used motor oil generally contains metal contaminants, samples of flue gas particulate collected at each site were analyzed for trace metals. Table 4 presents data on the concentrations of metals in the flue gas of the six boilers. As can be seen from Table 4, concentrations of lead and zinc in the flue gas were quite high. Lead emissions at levels described in Table 4 could cause violations of ambient air quality standards. Average particulate emissions at the six sites were 0.73 lb/hr or 0.34 lb/10^6 Btu heat input. This is higher than the average value for commercial boilers firing residual oil. The higher particulate emissions from the waste oil firing are most likely due to the higher ash content of the waste oil (0.15 to 1.5 percent). Particulate sizing measurements indicated that over 80 percent of the particulate matter containing lead are in the submicron size and range.

The flue gas emissions of HCl from the six boilers averaged 2.6 lb/hr. This is below the 4.0 lb/hr air emissions standard established for hazardous waste incinerators.

In summary, while the levels of organic emissions from the commercial boiler burning waste oil were not high, the boilers did not achieve a 99.99 percent destruction efficiency for the organic "spike" compounds. However, emission levels of inorganic compounds, particularly metals, are of greater concern than are those of organic compounds.

Combustion Of Hazardous Waste Materials In Industrial Boilers

There are roughly 43,000 industrial boilers in the United States with capacities larger than 10 million Btu/hr. Of this population, 5,500 boilers are located in the chemicals, petroleum refining, and paper industries. These 5,500 boilers are accessible to about 70 percent of total hazardous waste generated and over 95 percent of all potentially combustible hazardous waste generated in the United States. Thus, there exists considerable potential for on-site boiler combustion of much more than the 3.5 million metric tonnes of hazardous waste materials that are currently disposed of in boilers (7).

Because of the widespread utilization of industrial boilers for hazardous waste materials disposal and because of the existing exemption for boilers from the hazardous waste incinerator regulations, EPA conducted a series of 42 hazardous waste combustion tests at 11 full-scale industrial boilers. The boilers ranged from small gas-fired firetube boilers (approximately 10 million [MM] Btu/hr) to large pulverized coal watertube boilers (250 million Btu/hr). Waste fuel input ranged from less than 1 percent to 100 percent of fuel input.

Table 5 describes the test site boilers, the primary fuels, and the waste fuels typically fired (8). Most of the boilers were already burning solvent wastes or process production bottoms. In order to test the ability of the boilers to destroy difficult wastes and to facilitate comparisons between boilers many of the wastes were "spiked" with a chlorinated mix of waste compounds. The spike mixture consisted of carbon tetrachloride, 1,1,2 trichloroethylene (TCE), and chlorobenzene (Clϕ).

Table 6 presents the test site specific DREs for the waste compounds burned in the industrial boiler test program. Table 7 presents the industrial boiler

TABLE 3. CALCULATED DESTRUCTION AND REMOVAL EFFICIENCIES FOR WASTE OIL/COMMERCIAL BOILER TESTS

COMPOUND	DESTRUCTION AND REMOVAL EFFICIENCIES (PERCENT) MINIMUM	MAXIMUM	AVERAGE
Chloroform	99.65	99.96	99.88
Trichloroethane	99.37	99.97	99.80
Trichloroethylene	99.45	99.92	99.82
Perchloroethylene	99.73	99.96	99.84
Trichlorobenzene	99.84	99.98	99.92
Dichloronaphthalene	99.92	99.98	99.95
2,4,5-Trichlorophenol	99.92	99.99	99.97

TABLE 4. METALS EMISSIONS FROM COMMERCIAL BOILERS BURNING WASTE OIL

METAL	CONCENTRATION IN OIL (ppm)	EMISSION RATES ($\mu g/m^3$) MININUM	MAXIMUM	AVERAGE	AVERAGE EMISSION RATE (lb/hr)
Arsenic	6.9	11.2	655	223	*
Cadmium	1.4	8.3	350	126	*
Chromium	6.3	62.2	263	173	*
Lead	1550.0	5390	72400	34762	.12
Zinc	760.0	3134	33700	17981	.06

*Insignificant

DREs on a compound-specific basis.

It should be noted that only at test sites A and F were the average mass weighted DREs for all POHCs below the 99.99 percent required by the RCRA incinerator regulations. Phenol, pentachlorophenol, and naphthalene were the only waste compounds for which the required average DRE was not achieved. However, the poor DRE results for all three of these compounds are strongly influenced by the poor performance of boiler A. Note that the DREs for phenol at site C were all above the 99.99 percent level. The poor DRE performance at site A is most likely a characteristic of the wood-fired stoker design. The boiler at site F suffered from the fact that the burner operation was inadequate for the waste fuel being burned.

The introduction of waste fuels into the boilers did not appear to have a significant impact on criteria emissions, such as CO, NO, and particulate emissions. Total emissions of hazardous combustion byproducts, commonly referred to as Products of Incomplete Combustion (PICs) were about one order of magnitude or greater than total POHC emissions. Chloromethane, methylene chloride, and chloroform accounted for more than 75 percent of the total chlorinated PICs. Toluene contributed the bulk of total nonchlorinated PICs. A general trend of lower PIC emissions with higher POHC DREs was identified from the available test data. This suggests that combustion conditions leading to more efficient POHC destruction are also likely to result in lower PIC formation.

Hazardous Waste Combustion In A Lime Kiln

The production of lime involves the calcination of limestone at temperatures of approximately 2300°F (1260°C) in either rotary kilns or vertical shaft furnaces.

In 1980, there were 153 plants in the United States. These plants produced 18.1 million tons of lime (16400 Gg). Figure 1 is a schematic diagram of a lime kiln process (9).

Lime production is extremely fuel-intensive, requiring the consumption of 8.5 million Btu's of primary fuel to produce one ton of lime (9990 MJ/MT). Therefore, it would appear that lime kiln operators would be interested in less expensive fuel sources.

As part of the program to evaluate the combustion of hazardous waste materials in industrial processes, EPA tested a full-scale rotary lime kiln. The kiln, similar to that shown in Figure 1, was 8 feet in diameter by 220 feet long. The kiln rotated at one revolution per minute. It had a gentle (six percent) slope. The kiln had a countercurrent flow pattern (i.e., solid materials travel down the kiln and hot gases and dust emissions flow up the kiln). The lime product was produced at a rate of 17,000 lb/hr (7720 kg/hr) (9).

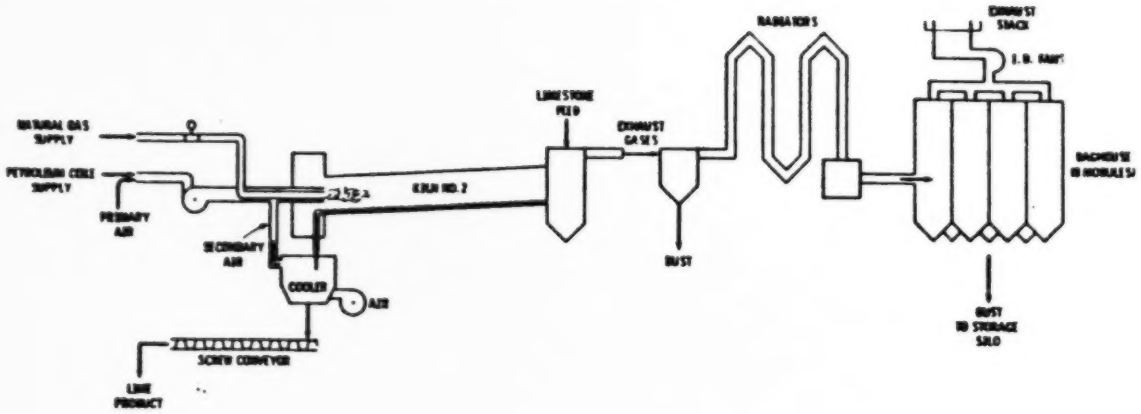

FIGURE 1: SCHEMATIC DIAGRAM OF A LIME KILN PROCESS

TABLE 5. DESCRIPTION OF TEST SITE INDUSTRIAL BOILERS

SITE	BOILER TYPE	CAPACITY MMBtu/hr	PRIMARY FUEL	TYPICAL WASTE FUELS	CONTROL DEVICE
A	Watertube Stoker	10	Wood Waste	Creosote Sludge	Multiclone
B	Packaged Firetube	8.5	Natural Gas	Alkyd Wastewater	None
C	Field Erected Watertube	230	Gas or Oil	Phenol Waste	None
D	Converted Stoker	90	No. 6 Oil	Methanol, Toluene Chlorinated Organics	None
E	Packaged Watertube	110	No. 6 Oil	Methyl Methacrylate Byproducts	None
F	Converted Watertube	60	No. 6 Oil, Gas, Propane	Paint Solvents	None
G	Modified Firetube	40	None	Highly Chlorinated Organics	2 Scrubbers In Series
H	Tangentially Fired Watertube	250	Pulverized Coal	Methyl Acetate	ESP
I	Packaged Watertube	62	Natural Gas	Aniline Waste In Nitrate Organics	None
J	Packaged Firetube	10	None	Toluene, Chlorinated Organics	None
K	Packaged Watertube	60	No. 6 Oil	Blended Waste With Light Oil	None

During baseline conditions, a blended combination of petroleum coke and natural gas was used to fire the kiln. During the waste fuel runs, a temporary 1-inch diameter stainless steel pipe was placed on the burner pipe and its nozzle pointed into the flame and the waste fuel and petroleum coke were fed unblended into the kiln.

The hazardous waste fuel was temporarily stored in a 5000 gallon tanker during the test burn. Additional chlorinated organics (tetrachloroethylene and trichloroethylene) were spiked into the waste fuel prior to the test to bring the total chlorine content to 3.0 percent.

Table 8 describes the DREs achieved for the POHCs used in the lime kiln test burn. Only methylene chloride had an average DRE below 99.99 percent and it is believed that the problem with this compound is more likely laboratory contamination rather than actual POHC emissions breakthrough. For the "spike" compounds (trichloro- and tetrachloro-ethylene) and for toluene, measured DREs were above 99.999 percent for all test runs.

Table 9 describes the impact of the waste fuel firing on criteria emissions from the kiln. As would be expected, HCl and particulate emissions increased. The high average CO emissions were more the result of frequent excursions rather than absolutely higher CO levels.

For a process such as a lime kiln, product quality is often more important than cost savings achieved through feed substitution. During the short span of the testing program it was not possible to explore operating conditions that could result in consistent product quality during waste firing. For this lime kiln test, consistent kiln operation could not be maintained and product quality occasionally suffered.

CONCLUSIONS

Six commercial boilers burning waste oils, 11 industrial boilers burning hazardous wastes, and 1 lime kiln are not an exhaustive sample of the universe of thermal processes that can be used to destroy hazardous wastes. However, based on the tests described here, some conclusions can be drawn.

1. Commercial boilers are not acceptable processes for combustion of waste oils that contain metals and chlorinated organics at the levels used in this test program. The levels of emissions of metals, particularly lead, are sufficiently high to offset gains in fuel costs savings. In addition, the organic waste destruction efficiencies (DREs) achieved by the commercial boilers were below the RCRA incinerator requirements. .

2. Industrial boilers are generally acceptable devices for hazardous waste destruction. Solvents, process bottoms with low ash contents, and even low concentrations of halogenated organics can be destroyed sufficiently to achieve the performance mandated by the RCRA incinerator regulations.

3. Wood-waste-fired stoker boilers present combustion environments that are too unstable for reliable hazardous waste combustion.

TABLE 6. TEST SITE SPECIFIC DREs FOR INDUSTRIAL BOILERS

SITE	COMPOUNDS (POHCs) BURNED	DREs MININUM	DREs MAXIMUM	DREs AVERAGE
A	Phenol, Pentachlorophenol, Fluorene, Naphthalene	99.5	99.9998	99.98
B*	Toluene	-	-	99.991
C	Phenol	99.998	99.9999	99.9996
D	Toluene, Perchloroethylene	99.994	99.9999	99.998
E**	CCl_4, TCE, Clϕ, MMA	99.95	99.9999	99.995
F**	CCl_4, TCE, Clϕ, Toluene	99.90	99.999	99.98
G	CCl_4	99.995	99.999	99.998
H	CCl_4, Trichloroethane, Clϕ	99.97	99.9996	99.991
I**	CCl_4, TCE, Clϕ, Benzene, Toluene Nitrobenzene, Aniline	99.97	99.99992	99.998
J**	CCl_4, TCE, Clϕ, Toluene	99.8	99.99993	99.9990
K**	CCl_4, TCE, Clϕ, Benzene, Toluene	99.996	99.99996	99.9997

*One test only.
**Spike mixture employed.
Clϕ = Chlorobenzene
MMA = Methylmethacrylate
TCE = Trichloroethylene

4. None of the wastes fired in industrial boilers contained metals. There is little evidence that high metallic wastes are burned in boilers. Therefore, in the absence of data, it is appropriate to conclude that wastes with metals contents above those stipulated in EPA's proposed waste oil regulation should not be burned in industrial boilers.

5. Lime kilns are capable of achieving satisfactory waste destruction. However, in the one test that is reported here, steady operation consistent with acceptable product quality was not achieved. It is possible that any operational changes that would be required to achieve consistent product quality when waste is fired would result in waste destruction as efficient as that reported here. However, further testing of this technology is required to verify that acceptable waste destruction can be achieved when a satisfactory product is created.

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TABLE 7. COMPOUND SPECIFIC DREs FOR INDUSTRIAL BOILERS

COMPOUND	SITES	DREs		
		MINIMUM	MAXIMUM	AVERAGE
Carbon Tetrachloride	E, F, G, H, I, J, K	99.97	99.9998	99.9992
1,1,2 Trichloroethylene	E, F, I, J, K	99.98	99.99993	99.9994
Chlorobenzene	E, F, H, I, J, K	99.8	99.99992	99.992
1,1,1 Trichloroethane	H	99.97	99.9996	99.994
Toluene	B, D, E, F, I, J, K	99.90	99.99996	99.998
Benzene	I, K	99.97	99.996	99.990
Perchloroethylene	D	99.994	99.9992	99.998
Methyl Methacrylate	E	99.95	99.997	99.991
Phenol	A, C	99.5	99.9999	99.977
Pentachlorophenol	A	99.97	99.998	99.98
Fluorene	A	99.98	99.9998	99.998
Naphthalene	A	99.94	99.995	99.98
Nitrobenzene	I	99.9999	99.99998	99.99996
Aniline	I	99.994	99.9996	99.9995

TABLE 8. DREs ACHIEVED IN LIME KILN

POHC	CONCENTRATION IN WASTE (WT%)	DRE		
		MINIMUM	MAXIMUM	AVERAGE
Methylene Chloride	0.11	99.60	99.999	99.983
Methyl Ethyl Ketone	2.69	99.998	99.999	99.999
1,1,1 Trichloroethane	0.24	99.989	99.999	99.997
Trichloroethylene	1.84	99.999	99.999	99.999
Tetrachloroethylene (PERC)	2.26	99.999	99.999	99.999
Toluene	11.6	99.999	99.999	99.999

TABLE 9. AVERAGE STACK EMISSIONS FROM LIME KILN

EMISSIONS	BASE FUEL ONLY	BASE FUEL AND WASTE
Particulates		
mg/dscm	28.7	35.3
kg/hr	0.9	1.0
HCL, ppm	2.0	4.4
SO_2, ppm	553	596
NO_x, ppm	386	446
CO, ppm	477	599
THC, ppm	8.2	3.5